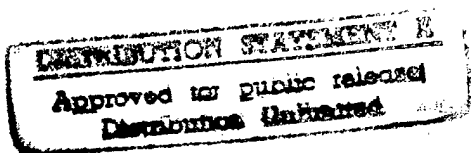


# **Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings**

**Year 1  
Quarterly Report No. 3  
March 19, 1996**



for Dr. Harold Guard (ONR) and Dr. Thomas Moran (ARPA)  
Contract #N00014-96--0147

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James O. Stoffer, and Professor Harlan Anderson

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**Title:**                    *Organo-Aluminate Polymeric Materials as Advanced Erosion/Corrosion Resistant Thin Film Coatings*

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**Sponsor:**            Defense Advanced Projects Research Agency  
                         Dr. Thomas Moran, Project Sponsor

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## **Proprietary Sections**

The information contained on pages 5-16 is considered proprietary. TDA and its team members will file invention disclosures with the Office of Naval Research on the research performed and will also file patent applications for the technologies described on pages 5-16 when development of the technologies are fully reduced to practice.

### **1. Executive Summary**

The goal of this three year DARPA project is the identification, preparation and application of chromate-free alumoxane-based durable coatings that provide a high level of corrosion resistance with low VOC and HAP emissions. The coating system is being designed for repair and maintenance of corrosion/mission coatings on existing DoD aircraft inventories. In the third quarter of the first year of this ARPA project, we have continued the syntheses of alumoxane-epoxy, alumoxane-urethane and phosphonato-alumoxane precursors that can be used to prepare durable alumoxane based coatings. In this quarters work we have also begun to evaluate alumoxane-

epoxy and alumoxane-urethane resins as coatings on aluminum substrates. In addition, cerium/molybdenum exchanged alumoxanes were prepared as precursors for the preparation of corrosion resistant oxide barrier coatings.

TDA has prepared difunctional (i.e. the organic groups contain two reactive -OH sites) alumoxanes precursors that can be readily converted into both alumoxane-epoxy and alumoxane-urethane polymers. These materials were converted into epoxy and urethane resins and then spray-coated onto 2024-T3 and 7075-T6 substrates. Using metal-exchange procedures developed at TDA, in conjunction with Professor Barron's group, we have also prepared cerium/molybdenum precursors that will be used to prepare potentially corrosion resistant oxide barrier layer films on clean aluminum substrates. Professor Anderson has been developing low temperature coating techniques for fabrication of corrosion resistant oxide barrier layers. Professor Stoffer's group has been developing techniques for incorporation of the alumoxane precursors into commercial coating formulations and evaluating the coatings using electrochemical impedance spectroscopy. Professor Barron's group has been evaluating the use of diacid cross-linkers for the fabrication of alumoxane coatings that do not containing reactive functional groups. Efforts are ongoing in Professor Barron's group towards the development of organophosphorus-alumoxane coatings for aluminum substrates.

## 2. Project Description

The primary goal of the DARPA program is the development of carboxylato-alumoxane based coating systems for repair and maintenance of DoD aircraft coatings. The proposed coating systems can potentially offer improved durability and corrosion protection, while avoiding the use of chromates and minimizing the emissions of both volatile organic compounds (VOC) and hazardous air pollutants (HAPs). The coating system is based on the development of carboxylato-alumoxane precursors for fabrication of corrosion resistant oxide barrier layers and alumoxane based primer coats and topcoats. The carboxylato-alumoxane precursors will be used to fabricate a corrosion resistant oxide barrier layer followed by an alumoxane-epoxy primer coat (Figure 1). A tie-coat will then be applied and an alumoxane-urethane added.

Fabrication of the oxide barrier coatings will be prepared using carboxylato-alumoxane precursors that have been metal-exchanged with molybdenum and cerium cations, and then applied to clean aluminum surfaces using plasma spray techniques. Previous work by several research groups (Mansfeld et al. 1991, Shaw et

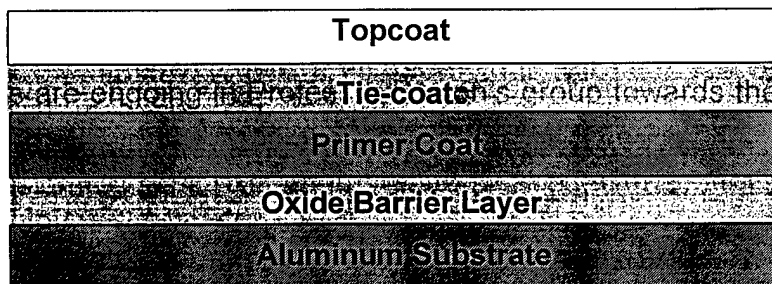


Figure 1. Schematic of coating system for aerospace applications.

al. 1990) has shown that cerium and molybdenum doped aluminum oxide barrier coatings offer exceptional corrosion resistance for aluminum substrates. Using selected functionalized carboxylato-alumoxanes, alumoxane-epoxy coatings will then be applied to the oxide barrier layer. A conventional tie-coat layer will be applied followed by an alumoxane-urethane layer. The carboxylato-alumoxane based coatings are anticipated to offer superior wear resistance and improved barrier properties compared to existing aerospace coatings.

Carboxylato-alumoxanes are low-cost nanocomposite (50-100nm) materials prepared from the reaction of carboxylic acids and the mineral boehmite ( $\text{AlO}(\text{OH})$ ), ~\$1/lb). The carboxylic acids are bound to the surfaces of the boehmite particles (Figure 2).

The covalently bound carboxylic acid groups confer unique properties to the boehmite particles. Previous work at TDA Research, Inc. (TDA) and by Professor Barron's group (Rice University) has shown that the attached carboxylic acids allow room temperature metal-exchange reactions to be carried out with the carboxylato-alumoxanes. The metal-exchanged (Ce/Mo) carboxylato-alumoxanes will be used to fabricate corrosion resistant oxide barrier coatings on the aluminum surfaces. Functionalized carboxylato-alumoxanes with amine or hydroxyl groups will then be prepared and converted to alumoxane-epoxies (using commercial epoxy resins) and alumoxane-urethanes (using commercial diisocyanates). We will utilize waterborne coating formulations for both the alumoxane-epoxy and alumoxane-urethane coating formulations.

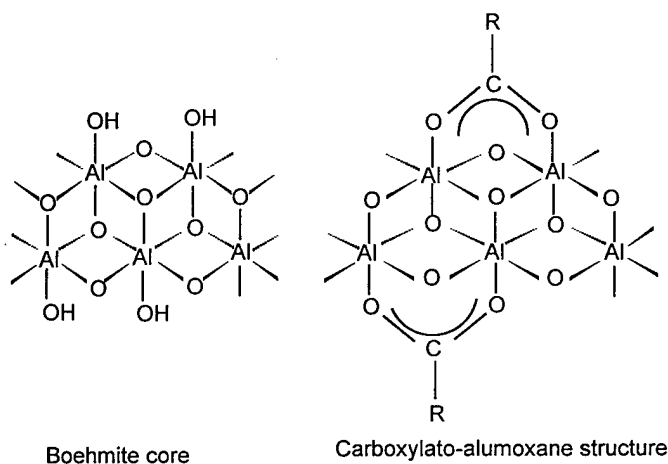


Figure 2. Comparison of the core structures of boehmite and the carboxylato-alumoxane

### 3. Research Results (December 19 (1996) - March 19 (1997))

#### 3.1. Research Progress

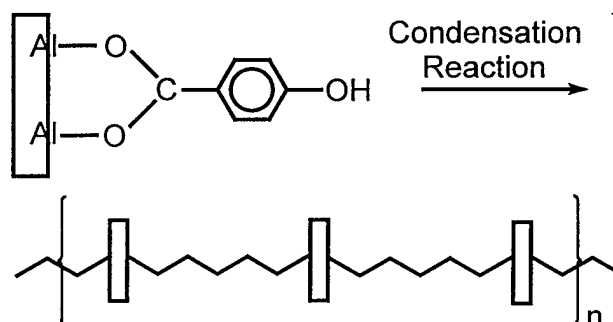
This quarters report is divided into three sections. In the first section we present results from our continuing efforts to prepare alumoxane precursors that can be used to fabricate durable corrosion resistant coatings on aluminum substrates. We also discuss syntheses of alumoxane-epoxy and alumoxane-urethane resins that are being evaluated for coatings on the aluminum. In the second section, we discuss TDA's efforts to prepare alumoxane-epoxy and alumoxane-urethane coatings, Professor Barron's work on the development of diacid cross-linkable coatings and organophosphorus coatings, and Professor Stoffer's efforts to incorporate alumoxanes

into formulated coatings using commercially available resins, cross-linkers, defoamers, surfactants and other additives. In the third section, we present the results of efforts towards development of corrosion resistant oxide barrier coatings by Professor Anderson and TDA.

### 3.2. Synthesis of Coating Precursors

In this quarter we have continued our efforts to prepare carboxylato-alumoxane precursors for use in the fabrication of alumoxane-epoxy primer coatings and alumoxane-urethane topcoats. In our previous quarterlies, we presented results using the monofunctional 4-hydroxybenzenato-alumoxanes as precursors for both the epoxy and urethane coatings. In this quarter we have prepared difunctional alumoxanes as precursors for preparation of the epoxy and urethane coatings. Figure 3 shows a schematic of "polymer resins" prepared using monofunctional versus difunctional alumoxane precursors. We anticipate that coatings prepared using the difunctional alumoxane precursors may offer superior performance over the coatings prepared using the monofunctional alumoxane precursors. For example, resin coatings prepared using the bifunctional alumoxanes will allow formation of long chain polymer structures that are bound together with short alumoxane cross-linked segments. Such structures are expected to improve both the flexibility and the mechanical stability of the alumoxane coatings. If the carboxylate bond to the boehmite particle is broken, the particle will remain entrapped within the continuous polymer backbones. The use of a long polymer backbone also allows more flexibility for modifying the properties of the alumoxane-polymer-resins. The difunctional alumoxane precursors are also expected to lead to better orientation of the boehmite particles. Enhanced orientation of the boehmite particles is expected

Monofunctional Alumoxane Condensation Polymer



Bifunctional Alumoxane Condensation Polymer

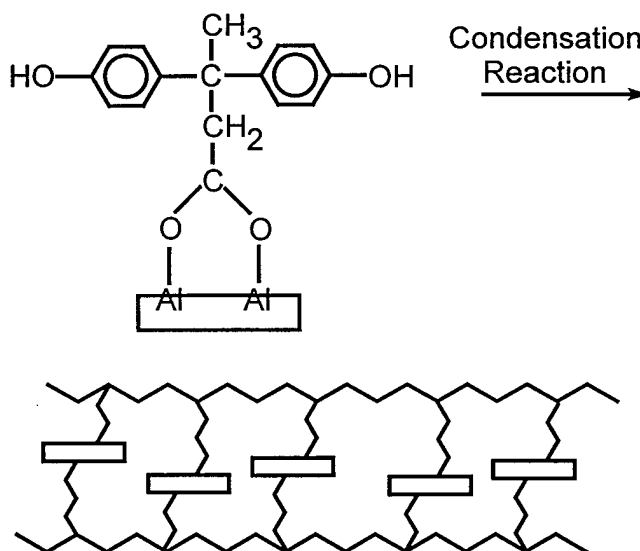


Figure 3. Schematic of polymers formed with monofunctional and bifunctional alumoxane precursors

to provide better wear resistance and reduced permeation of water and oxygen.

### Synthesis of Difunctional Alumoxane-Epoxyes

Epoxyes are well known for their excellent adhesion to a variety of substrates. They also form hard and tough coatings for architectural, automotive and aerospace applications. We have previously reported the preparation of alumoxane epoxyes using monofunctional hydroxybenzoic acid (HBA) alumoxane and the diglycidyl ether of bisphenol A (DGEBA, commercially available as Dow Chemical Co. product DER 332). In our previous quarterly we reported the syntheses of difunctional alumoxanes using the carboxylic acids diphenolic acid (DPA) and dimethylolpropionic acid (DMPA). In this quarter we have prepared epoxyes and urethanes using the bifunctional alumoxanes. The syntheses are described below.

Preparation of DPA alumoxane diglycidyl ether In a round bottom flask 7.00g (0.037 mol) DGEBA waxy solid was dissolved in 50mL dimethoxyethane. While stirring, 2.02g diphenolic acid (DPA) alumoxane and 30 $\mu$ L of the catalyst 1-imidazole were slowly added (Figure 4). The mixture was then heated under reflux for five hours at 80°C.

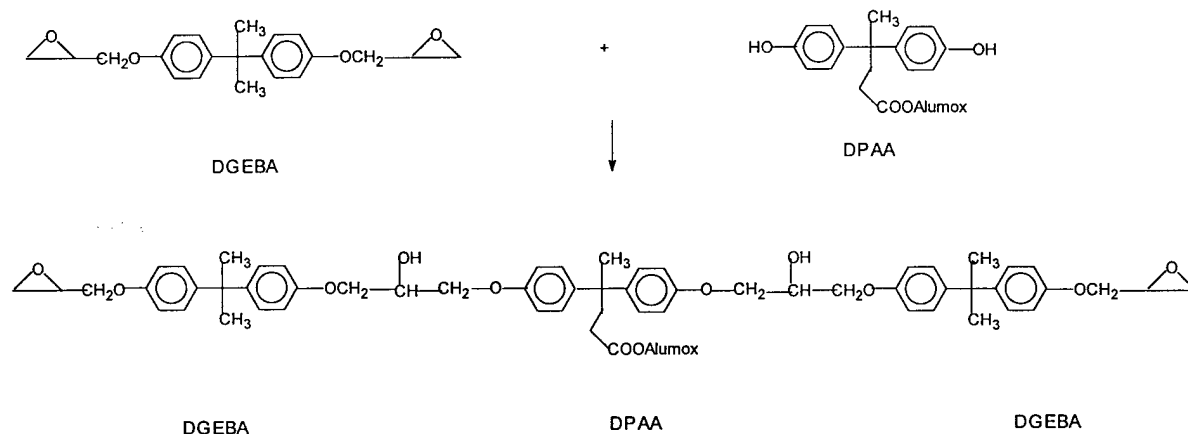


Figure 4. Preparation of the epoxy component of diphenolic acid alumoxane

FTIR analysis of the alumoxane solution is presented in Figure 5 for the mixture before the chain extension reaction and for the mixture after the five hour reflux. The absorbance at 936  $\text{cm}^{-1}$  remained the same, indicating that the concentration of oxirane rings (epoxy groups) remained unchanged and that the system was ready for curing with the amine. However, the reduction in the absorbance at 1073  $\text{cm}^{-1}$  may be an indication that the alumoxane system added to the secondary hydroxyls of DGEBA as a side chain as well as a linear extension of the commercial epoxy. This was not expected to influence curing. Application of this material to the 7075-T6 aluminum substrates is described in the coatings section.

Preparation of DMPA diglycidyl ether alumoxane A similar synthesis procedure was used to prepare the aliphatic DMPA alumoxane epoxy. A solution of 1.85 g (5mmol) DGEBA

(DER 332) in dimethoxyethane was mixed with 1.20 g (53mmol) DMPA alumoxane and 30 $\mu$ L 1-imidazole and heated for 30 minutes. Tris-(2-amino-ethyl)amine was used as the curing agent and was added to the sample prior to coating an aluminum (7075-T6) substrate.

#### Preparation of DMPA and DPA Alumoxane Epoxy Using Cyclo-aliphatic Epoxy Resins

To avoid the formation of brittle films and the cracking and peeling of the alumoxane films from the aluminum substrates it is necessary to design flexibility into the alumoxane-epoxy coatings. The DMPA-alumoxane

epoxies are anticipated to be more flexible than the DPA-alumoxanes that contain the aromatic rings. Similarly, the substitution of an aliphatic diglycidyl-ether is expected to enhance film flexibility. To optimize the barrier properties, chemical resistance and flexibility of the alumoxane-epoxy coatings it may be necessary to mix and match the alumoxanes and the diglycidyl-ethers. We have therefore prepared alumoxane-epoxies using the cyclo-aliphatic di-epoxy precursor whose structure is shown in Figure 6.

To prepare the cyclo-aliphatic alumoxane epoxy we mixed 1.9 g (7.5mmol) of the cyclo-aliphatic epoxy resin (Union Carbide ERL 4221) with 1.0 g of the DMPA-alumoxane and 30 $\mu$ L of 1-methylimidazole (a base catalyst) and the mixture was heated for an hour. With this formulation the

mixture formed a gel. Another solution was prepared with 0.60 g DPA alumoxane and 0.8 g (3.2 mmol) of the cyclo-aliphatic epoxy resin and 30 $\mu$ L 1-imidazole. With this formulation the solution components remained suspended in the solvent.

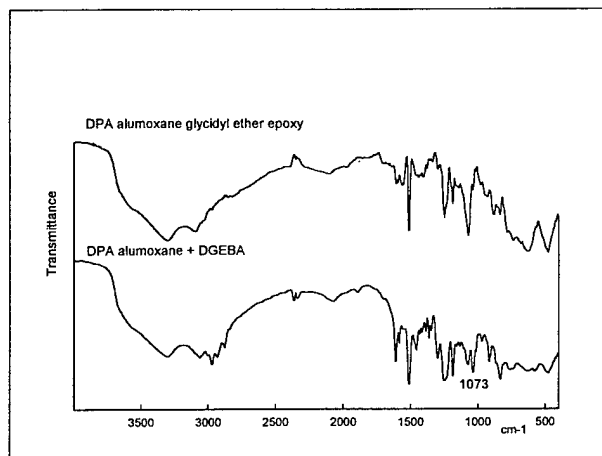


Figure 5. FTIR of the conversion of DPA alumoxane to an epoxy

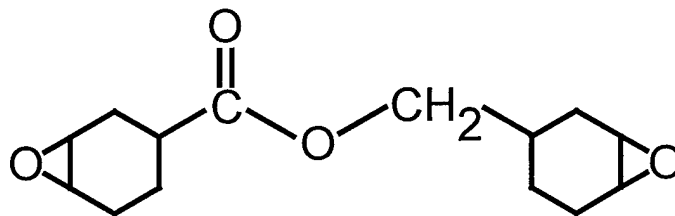


Figure 6. Structure of the cyclo-aliphatic epoxy resin ERL 4221

#### **Synthesis of Difunctional Alumoxane-Urethanes**

Due to their favorable balance of properties (chemical resistance, toughness, abrasion resistance and weathering), urethanes have gained widespread use as coatings. In order to improve the abrasion resistance and barrier properties of the urethane topcoats, we have begun to prepare alumoxane-urethane resins and alumoxane-urethane coatings.



The alumoxane-urethanes were prepared using the difunctional DMPA- and DPA-alumoxanes. The DMPA-alumoxane urethanes were prepared as two component formulations with DMPA and methylene bis-(4,4'-phenylene diisocyanate) (MDI). In a round bottom flask 25.2g MDI was dissolved in 40 mL methyl isobutyl ketone (MIBK) by heating for 10 minutes. In a separate flask, 5.2 g of the DMPA alumoxane was mixed with 40 mL of dimethylsulfoxide (DMSO) for 10 minutes and the slurry was added to the MDI

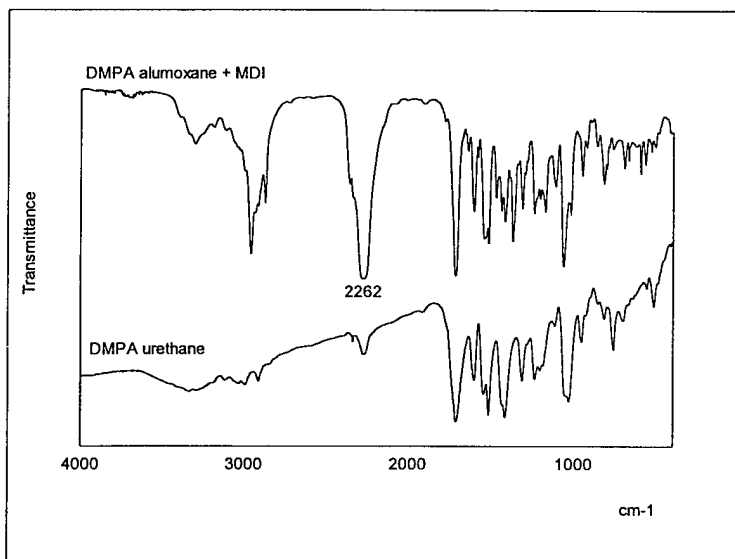


Figure 7 FTIR of the DMPA-alumoxane-urethane

solution. The two-component mixture was heated to reflux for 30 minutes until the viscosity increased. The mixture remained cloudy and homogeneous. Two other preparations were made by varying the reaction time to include 15 minute and 75 minute reflux periods.

The viscosity of the sample heated for only 15 minutes was too low for spraying of even coatings, whereas the mixture heated for 75 minutes gelled and therefore could not be sprayed. The FTIR spectra shown in Figure 7 confirms the formation of the urethane by the disappearance of isocyanate absorption at  $2262\text{ cm}^{-1}$ . The DMPA-alumoxane-urethane solutions prepared using a 30 minute heating cycle were suitable for spray coating of the aluminum substrates. A similar procedure was carried out using DPA alumoxane as the difunctional alumoxane for the preparation of urethane coatings.

In summary, we have prepared a number of alumoxane-epoxies and alumoxane-urethanes using the difunctional alumoxane precursors. With these materials we have started to prepare alumoxane-epoxy and alumoxane-urethane coatings on aluminum substrates. These preliminary experiments, and their results, are presented in the next section.

### 3.3. Preparation of Carboxylato-Alumoxanes Coatings

In this section we present the results of our initial efforts at coating aluminum substrates using alumoxane based coatings. We report on the preparation of alumoxane-epoxy and alumoxane-urethane coatings at TDA, the preparation of di-acid cross-linked coatings and organophosphate-alumoxane coatings by Professor Barron's group, and the complex alumoxane containing coating formulations prepared by Professor Stoffer's group.

## Preparation of Alumoxane-Epoxy coatings

We have used the DMPA-alumoxane-epoxy and DPA-alumoxane-epoxy prepared in the previous sections for preparation of epoxy-coated aluminum substrates. The details of these efforts are given below.

Preparation of DPA- and DMPA-Alumoxane Diglycidyl-Ether Epoxy Resin Coatings - To 1.70g (0.035 mol) of the DPA-alumoxane diglycidyl ether prepared above, we added 1.8 g (0.037 amine equivalents) of the tris-(2-aminoethyl)amine curing agent and the mixture was heated for 30 minutes. The mixture was applied by airbrush onto the aluminum coupons and allowed to cure. Two curing processes were examined: room temperature curing for three days resulted in a soft, easily scratched film, while curing at 110°C for six hours produced a harder and more homogeneous coating. To determine whether sufficient cross-linking could be achieved using the alumoxane diglycidyl ether without the addition of the amine curing agent, a sample of the solution was applied to a coupon without addition of the amine curing agent and then heated at 110°C for six hours. The resulting coating was clear and homogeneous, but brittle. This result suggested that while a cross-linking agent was not absolutely necessary for film formation, the use of the curing agent resulted in higher quality films. Similar studies were also carried out using the alumoxane-epoxy prepared from the DMPA-alumoxanes. We observed that DMPA-alumoxane coatings were less brittle than those prepared with the DPA-alumoxane. For both coatings prepared using the amine curing agent, we observed the formation of clear, dense homogeneous coatings.

Preparation of DMPA-Alumoxane Cyclo-aliphatic-Ether Epoxy Resin Coatings - We have also prepared coatings using a mixture of the cyclo-aliphatic di-epoxy resin and the DMPA-alumoxane. The DMPA-alumoxane cyclo-aliphatic ether precursor was prepared as described above using the DMPA-alumoxane, the cyclo-aliphatic di-epoxy and the 1-methylimidazole catalyst. The curing agent tris-(2-aminoethyl)amine was then added to the solution and the mixture was sprayed onto the aluminum substrates. Following curing at 110°C for six hours a smooth thin film coating was formed. The FTIR spectrum of the cured film is shown in Figure 8. The disappearance of the oxirane ring (the peak at 936 cm<sup>-1</sup>) indicates reaction of the alumoxane-epoxy with the amine curing agent. An attempt to prepare thicker films resulted in some separation of components. This phenomena will be examined in more detail in the future.

Preparation of Diacid Cross-Linked Alumoxane Coatings - Professor Barron's group has evaluated the fabrication of coatings using long chain diacids to cross-link the alumoxanes and form

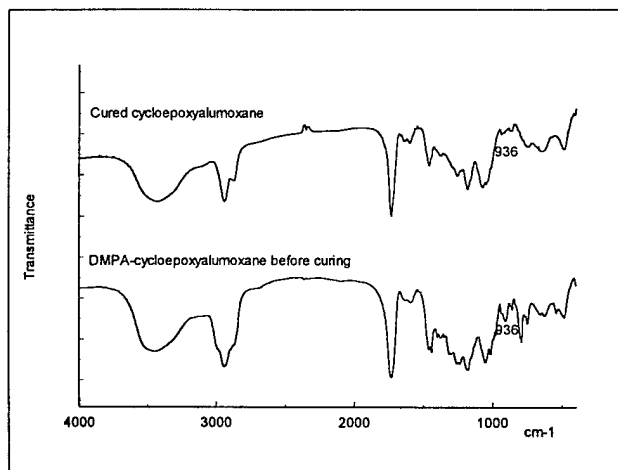


Figure 8. FTIR of cured and uncured DMPA alumoxane epoxy

alumoxane coatings. The coatings are prepared by the reaction of 2-ethylhexanato-alumoxanes and sebacic acid ( $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ ). The details of these efforts are described below.

Pseudo boehmite (20g) and 65 ml of 2-ethylhexanoic acid were mixed in 300 ml of xylene. The mixture was then refluxed gently for approximately 24 hours, at which time a thick, milky-white, gel had formed. Upon treatment with ethanol, the gel precipitated a "fluffy" white solid. The precipitate was filtered, washed with methanol, and dried. The ethylhexanto-alumoxane (2g) was then mixed with 0.5g of sebacic acid in 100mL of xylene. After heating gently for approximately 30 minutes, a thick, gray-white, gel formed. This gel was then used as a coating material. The coatings were homogeneous and scratch resistant (a hardness of about 7).

Preparation of Phosphonato-Alumoxane Coatings - Professor Barron's group has also prepared organophosphate-alumoxane coatings. These materials may impart corrosion resistance to the aluminum substrates due the presence of high levels of phosphorus in the coating materials that could react with solubilized  $\text{Al}^{3+}$  to form insoluble aluminum phosphates. Pseudoboehmite (10g) was mixed with 30ml of di-n-amylphosphate in 200mL of toluene. After approximately 12 hours, the mixture formed a thick, white gel. This gel could then be used to form adherent coatings that were clear in areas where the film thickness was small, and white in thicker areas. The thin, clear sections were impervious to scratching (to a hardness of at least 8).

#### **Formulation of Complex Alumoxane Containing Polymer Coatings**

Professor Stoffer's group has been evaluating the preparation and application of alumoxane precursors as corrosion inhibitors in typical corrosion coating formulations. The alumoxanes were used as one component of a complex mixture of epoxy resins, curing agents, defoamers, surfactants and dispersants. In particular, the alumoxanes are being evaluated as corrosion inhibiting materials

The raw materials used in the study are the EPI-REZ 5522-WY-55 waterborne epoxy resin and the EPI-CURE 8290-Y-60 water reducible amine curing agent (both from Shell). The additives, including defoamer BYK020, the surfactant and dispersant Disperbyk, were obtained from BYK company. Alumoxanes were provided by TDA. The pigments were: modified wollastonite from NYCO Mineral, Inc., water ground mica from KMG Minerals, Inc., and SPARMITE from Harcros Pigments Inc. A classical corrosion inhibitor, Halox SW-111, was used for preparation of comparison coatings.

Both 4-hydroxybenzenato-alumoxane and gluconato-alumoxane were used as the corrosion inhibitors in the water-based coating formulation. The nominally insoluble 4-hydroxybenzenato-alumoxane was added during the dispersion phase with the pigment additives. The soluble gluconato-alumoxane was dissolved in 50°C water. ZEEOSPHERES 400 from Zeelan Industries, Inc. were also added to the coating formulation.

Substrate Pretreatments - The aluminum substrate (Al 7075-T6) panels were obtained from Q-Panel Company. The panels were pretreated before being coated. They were first rinsed with acetone, and then immersed in the 5 wt% Turco alkaline cleaner solution at  $65 \pm 5^\circ\text{C}$  for 10 minutes to degrease. The cleaned aluminum panels were dipped in the deoxidizing solution which contained 2.5 wt% Amchem #11 and 10 vol%  $\text{HNO}_3$  for 3 minutes, and then rinsed with distilled water.

Coating Formulations - The coating formulations for the alumoxanes and Halox SW-111 are shown in Tables 1, 2, 3. These formulations are two part epoxy systems. Part A was prepared by first adding the defoamer and surfactant to the resin under stirring with a Cowles blade at 800 RPM. All the pigment was then slowly added under the same stirring speed. The solvent was added to adjust the viscosity of the paints. Once added, the speed was increased to 1200 RPM. Dispersion of Part B components was carried out by using ultrasonic mixing. Parts A and B were then mixed and dispersed at 1200 RPM for 30 minutes. The coatings were drawn down on the aluminum panels to give a wet film thickness of 6 mil. The panels were cured at  $50^\circ\text{C}$  for either 12 hours or 24 hours.

Corrosion Tests - All the panels were scribed and placed in the salt fog chamber for the corrosion test. Electrochemical Impedance Spectroscopy (EIS) were conducted. The EIS results are given as Figures 1-6 in Appendix 1. The initial coating formulations appear to have some degree of nonpermeability as interpreted from the EIS results. These data are preliminary however, and more in-depth studies will be carried out in the future.

### **3.4. Fabrication of Oxide Barrier Coatings for Aluminum Substrates**

In this quarter we have also began to evaluate several techniques for fabrication of a corrosion resistant oxide barrier layer on aluminum substrates. Preliminary evaluations of both plasma spray coating techniques and spin coating techniques have been evaluated in the for the fabrication of oxide barrier layers. In addition, we are developing cerium, molybdenum and cerium/molybdenum doped precursors that can used to prepare doped alumina oxide films on aluminum substrates. As discussed in greater detail below, cerium and molybdenum doped alumina oxide films offer exception corrosion resistance to aerospace (2024-T3, 6061-T3 and 7075-T6) aluminum materials

#### **Synthesis of Precursors for Ce/Mo Doped Alumina Protective Barriers**

Aluminum alloys containing copper (e.g. 2024-T3, 6061-T6 and 7075-T6) are important aerospace materials because of their high specific strength. Unfortunately, if left untreated the Al-Cu alloys will corrode at rates that are dependent on the alloy, the

Table 1 Waterborne epoxy coating formulation using Halox SW-111

Material	Weight(g)
<b>Part A</b>	
EPI-REZ 5522-WY-55	28.5
Diacetone alcohol	7.6
BYK020	1.0
Disperbyk 182	1.0
H <sub>2</sub> O	5.2
<i>- High Speed Mix -</i>	
10ES wollasokup	9.2
TiO <sub>2</sub> , R-900	6.1
Halox SW-111	8.6
Zeeospheres 400	6.1
Sparmite	6.1
Water ground mica, 325 mesh	0.7
<i>- High Speed Disperse -</i>	
EPI-REZ 5522-WY-55	12.7
H <sub>2</sub> O	1.2
<b>Part B</b>	
EPI-CURE 8290-Y-60	5.2
H <sub>2</sub> O	9.5
<b>Total</b>	110

Table 2 Waterborne epoxy coating formulation using 4-hydroxybenato-alumoxane

Material	Weight(g)
<b>Part A</b>	
EPI-REZ 5522-WY-55	28.5
Diacetone alcohol	24.1
BYK020	1.0
Disperbyk 182	1.0
H <sub>2</sub> O	5.2
- High Speed Mix -	
10ES wollasokup	9.2
TiO <sub>2</sub> , R-900	6.1
4-hydroxybenato-alumoxane	8.6
Zeeospheres 400	6.1
Sparmite	6.1
Water ground mica, 325 mesh	0.7
- High Speed Disperse -	
EPI-REZ 5522-WY-55	12.7
H <sub>2</sub> O	1.2
<b>Part B</b>	
EPI-CURE 8290-Y-60	5.2
H <sub>2</sub> O	9.5
<b>Total</b>	126.5

Table 3 Waterborne epoxy coating formulation using Gluconato-alumoxane

Material	Weight(g)
<b>Part A</b>	
EPI-REZ 5522-WY-55	28.5
Diacetone alcohol	4.2
BYK020	1.0
Disperbyk 182	1.0
H <sub>2</sub> O	5.2
<i>- High Speed Mix -</i>	
10ES wollasokup	9.2
TiO <sub>2</sub> , R-900	6.1
Gluconato-alumoxane	4.3
Zeeospheres 400	6.1
Sparmite	6.1
Water ground mica, 325 mesh	0.7
<i>- High Speed Disperse -</i>	
EPI-REZ 5522-WY-55	12.7
H <sub>2</sub> O	5.3
<b>Part B</b>	
EPI-CURE 8290-Y-60	5.2
H <sub>2</sub> O	9.5
<b>Total</b>	106.1

composition, and the local environment. Copper in the Al-Cu alloys increases pitting attack by the formation of galvanic couples. To arrest or significantly delay corrosion of the aluminum alloys a number of oxide barrier layer coating approaches have been developed. These approaches generally involve the formation of oxide barrier coatings on the aluminum substrate. In addition to offering corrosion protection to the aluminum substrate, the oxide layers also provide an effective adhesive base for protective organic coatings.

The most successful oxide barrier coatings for corrosion protection of aerospace aluminum have historically been based on the use of chromium compounds (Cohen 1995). The corrosion barriers prepared using chromate conversion coatings or chromic acid ( $\text{H}_2\text{CrO}_4$ ) anodization provide such a high level of corrosion protection that they are regarded as the "standard" corrosion inhibitors to which all others treatments are compared. Unfortunately, hexavalent chromium ( $\text{Cr(VI)}$ ) and its compounds are toxic and are becoming tightly regulated. The need to find environmentally acceptable replacements for chromium containing protective oxide films on aluminum substrates has spurred intensive efforts to identify environmentally compliant surface treatments.

Of the many alternative oxide barrier coatings, it has been found that oxide coatings incorporating cerium and molybdenum have been the most promising for control of aluminum corrosion. Mansfeld and coworkers (Mansfeld et al. 1991) have evaluated incorporation of molybdenum and cerium into the aluminum oxide films. The first step of this procedure involved immersion of the aluminum substrate into boiling aqueous cerium nitrate ( $\text{Ce(NO}_3)_3$  10 mM) solutions for two hours, followed by immersion in boiling aqueous cerium chloride ( $\text{CeCl}_3$  5 mM) solutions. The treated substrates were then anodized in a deaerated aqueous 0.1M  $\text{Na}_2\text{MoO}_4$  solution for two hours. Substrates modified in this manner did not show any signs of localized corrosion after 60 days immersion in 0.5N NaCl solution. A scratched sample did not show any signs of localized corrosion after 25 days immersion in the 0.5N NaCl solution. Shaw and coworkers (Shaw et al. 1990) showed that incorporation of molybdenum ( $\text{Mo}^{4+}$  or  $\text{Mo}^{6+}$ ) ions into the aluminum oxide barrier film also offers substantial protection against corrosion of the underlying aluminum substrate. For both approaches it is believed that cerium and molybdenum are incorporated into the aluminum oxide film formed on the surface of the aluminum substrate.

The inhibition of corrosion by cerium-doped aluminum oxide barrier layers is believed to operate by decreasing the rate of cathodic oxygen reduction. Molybdate-doped aluminum oxide barrier layers are believed to improve the localized corrosion resistance of aluminum and aluminum alloys by shifting the breakdown potential positively so that the open circuit potential is negative relative to the breakdown potential. The procedures described above (i.e. immersion plus anodization) may be a viable approach for pretreatment of small aluminum parts, but are not useful for repair and maintenance of aircraft coatings. Therefore, methods are needed to generate molybdenum/cerium doped aluminum oxide films to repair damaged areas on aircraft.



We have identified a potential route to the fabrication of the Mo/Ce doped aluminum oxide films on clean (i.e. sandblasted) aluminum surfaces. The new route (in development) utilizes the unique metal-exchange chemistry of the carboxylato-alumoxanes and the use of aqueous plasma spray coating techniques being developed by Professor Harlan Anderson at University of Missouri-Rolla. In this approach, we first prepare water soluble carboxylato-alumoxanes that have high ceramic yields. The alumoxanes are then metal-exchanged with Mo, Ce or both Mo and Ce using the metal acetylacetonate complexes of the two metals. The water soluble metal exchanged alumoxanes can then be used to prepare Mo/Ce metal exchanged aluminum oxide coatings by the aqueous plasma spray coating technique. Several aspects of the above procedure have been carried out, and the results are described below.

Small water soluble carboxylato-alumoxane particles were prepared by the reaction of acetic acid and boehmite in water (developed by Professor Barron's group). Pseudoboehmite (50g) was first slurried in water (500 ml) and then acetic acid (40mL) was added. The reaction mixture was stirred for five minutes and then centrifuged at 9000 rpm for 45 minutes. The solution was decanted off and the residual water was then removed overnight under vacuum at 80-90°C. The dry acetato-alumoxane powder was then washed with methanol and filtered. A second drying at 90°C was then carried out overnight and resulted in a water soluble white powder. Ceramic yields of the purified white acetato-alumoxane were found to be 73-78%. The material is water soluble and the particle size (measured using photon correlation spectroscopy) ranges from 3-100 nm, with the majority of particles being in the 30-60 nm range.

The acetato-alumoxane powder was then dissolved in water along with cerium (III) acetylacetonate in a ratio of 10:1 Al:Ce. The mixture was stirred at 50°C for two hours. The mixture was then filtered and the cerium exchanged acetato-alumoxane washed with methanol to remove the  $\text{Al}(\text{acac})_3$  formed by the reaction of the cerium acetylacetonate with the acetato-alumoxane. Heating the material to temperatures between 350-900°C resulted in the formation of cerium doped gamma alumina as verified by XRD and XRF analyses. The reaction of acetato-alumoxane with molybdenum (VI) acetylacetonate gave similar results. We are preparing larger quantities of these materials including a Ce/Mo doped alumoxane to deliver to Professor Anderson for plasma spray coating studies. We anticipate that high quality plasma sprayed Ce/Mo doped aluminum oxide barrier coatings will offer good corrosion protection.

### **Plasma Deposition of Alumina on Aluminum**

Professor Anderson has begun to carry out plasma spray coating procedures for fabrication of oxide barrier coatings on alumina substrates. Both dry powders and aqueous solution precursors are being evaluated. Initial studies have been carried out with dry powders of aluminum hydroxide. Plasma spraying of boehmite and Ce/Mo metal exchanged boehmite powders will be carried out next (March 19th-June 19th 1997) quarter. As discussed in the preceding section we anticipate that the Ce/Mo coatings will provide a corrosion resistant oxide barrier coating.

Initial studies by Professor Anderson's group were conducted using dry aluminum trihydroxide ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) produced by ALCOA Chemicals. The dry powders were fed into the plasma gun and sprayed onto a sandblasted alumina surface. The dry aluminum trihydroxide powders were 10-15 $\mu\text{m}$  agglomerates composed of 1-2 $\mu\text{m}$  powders (Figure 9). The morphology and structure of the deposited films were found to be dependent upon the gas used to create the plasma. When argon is used to form the plasma, the surface coating has a mixed structure as determined by x-ray diffraction. The coating was adherent, but porous.

A fully dense and adherent coating was obtained using a nitrogen and hydrogen mix to form the plasma (see Figures 10-12). A much higher heat transfer was obtained using the mixed gas plasma, and a water cooled holder was used to prevent melting the aluminum substrate. Deposited layers showed a layered-splat morphology indicating the powders were molten upon impact with the surface. A nano-crystalline crystal structure is indicated by the splat size with a plate thickness on the order of 100 nm. The surface topology was irregular, but may provide a good surface for bonding to an epoxy. Adherent layers, up to 10 $\mu\text{m}$  thick, have been successfully deposited on aluminum. These films consist of layered splats with a nano-crystalline structure. Grain diameters are on the order of 100-300 nm in size. These films appear to be fully dense when examined by SEM on metallographic cross-sections; however, the surface topology is irregular and appears porous. Structure analysis of the films is currently being conducted using both TEM and x-ray diffraction.

#### **Fabrication of Amorphous Ce and CeO<sub>2</sub> coating on Al substrates**

Professor Anderson's group has previously developed several routes to the synthesis of oxide films using ethylene glycol based precursor solutions. Preliminary studies of cerium oxide films formed using these precursors were carried out during this quarter. Initial solutions of a two mole percent cerium solution were prepared by the addition of cerium nitrate to ethylene glycol held at 75°C. The solution was held at 75°C for 72 hours in order to remove the residual nitrates awhile retaining the homogeneity of the solution. Spin coating this solution onto the aluminum substrates was carried out at 4000 rpm for 30 sec, followed by a 1 hour bake at 75 °C and a 2 hour anneal at 150°C. X-Ray diffraction patterns of the films, prepared using the above approach, showed the films to be amorphous (Figure 13). Initial coating studies were done on a 7075 Al substrate, and some studies were also conducted with 2024-T3 aluminum substrates.

When the cerium/ethylene glycol precursors were coated onto the 2024-T3 aluminum substrates, it was observed that some "staining" occurred in the samples during the 150°C anneal. This was not observed for the 7075-T6 aluminum substrates. It was assumed that due to the higher Cu content in the 2024-T3 aluminum substrates the residual nitrates in the solution would act as a catalyst for the oxidation of the Cu. Therefore the cerium precursor solutions were held for additional periods of 24, and 72 hours at 75°C resulting in total times of 96 and 144 hour holds. Spin coating these

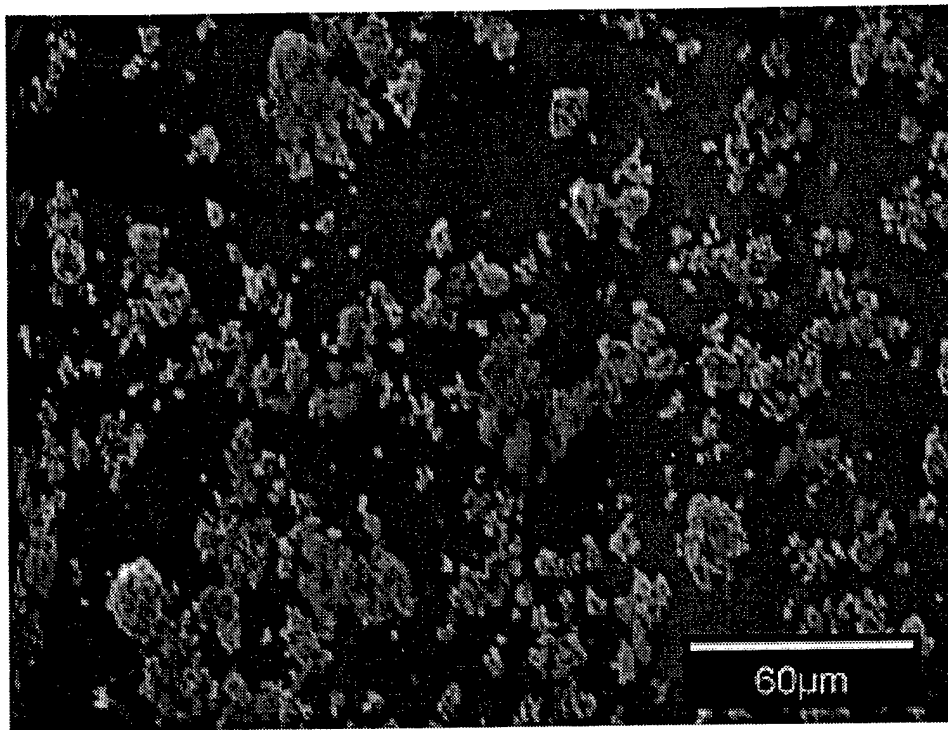


Fig. 9. SEM image of the as-received aluminum trihydroxide powders used for plasma spraying. Most powders are agglomerates of very fine powders 1-2  $\mu\text{m}$  in size.

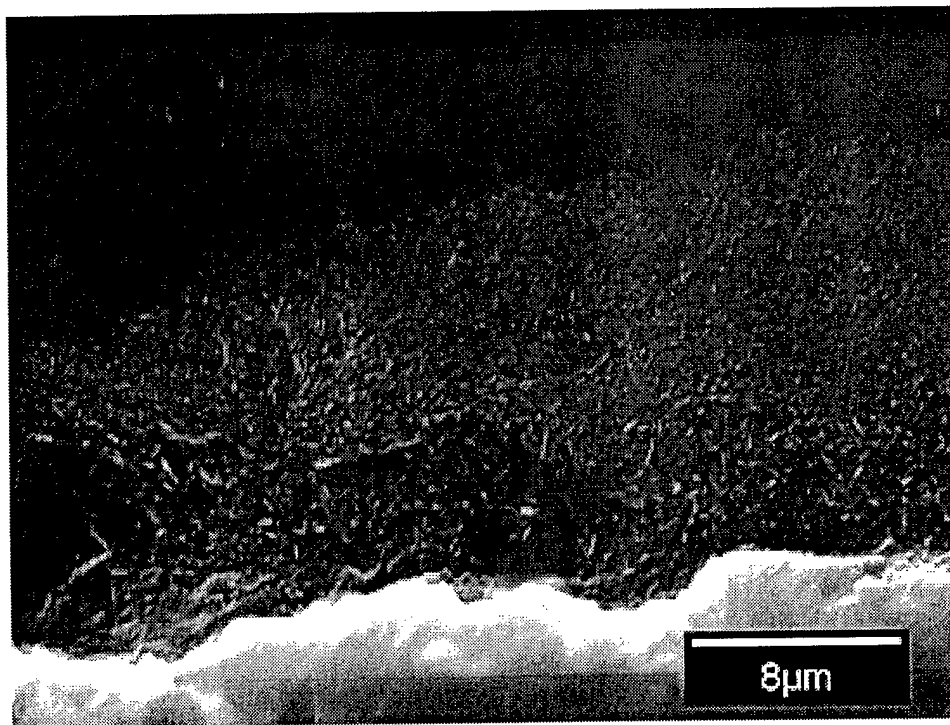


Fig. 10. SEM image of a cross-section prepared by standard metallographic techniques. The surface layer was damaged during preparation; however, the film is adherent to the substrate which is shown at the bottom of the figure.

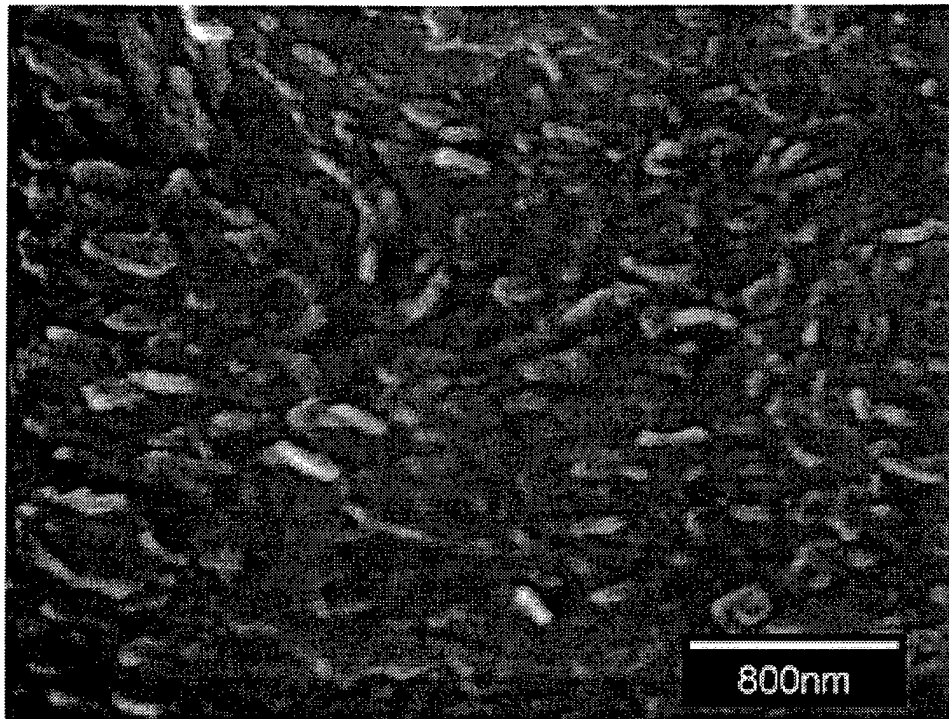


Fig. 11. An SEM picture of the alumina deposit. Sample was prepared by metallography. The structure consists of nanometer sized splats, indicating the powders were molten prior to impact.

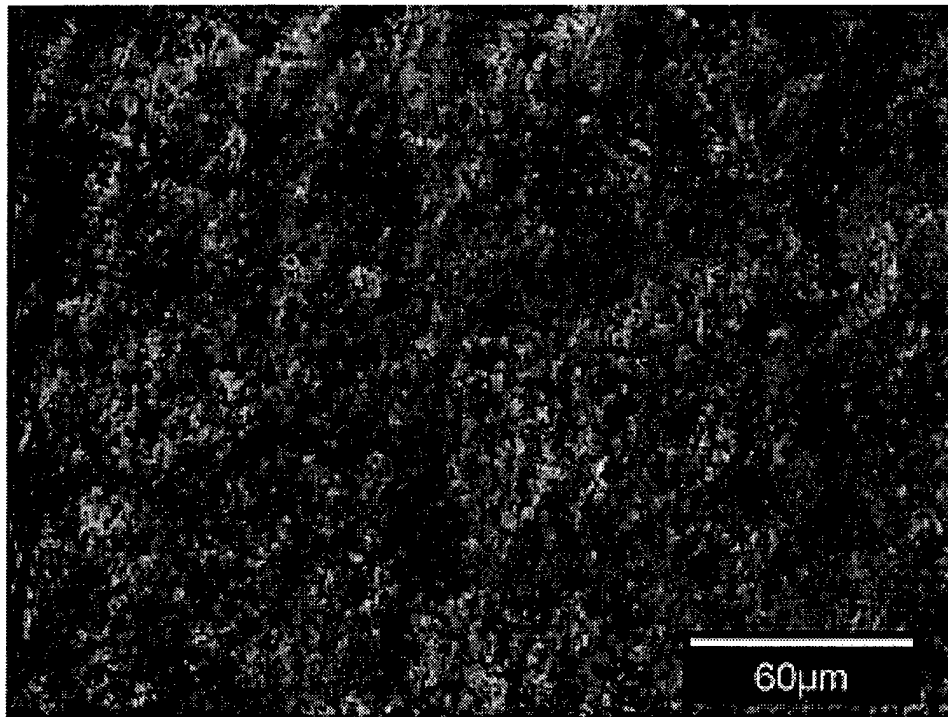


Fig. 12. SEM image of the deposited surface.

**3 Ce spin layers on 7075 Al  
solution prepared at 75°C for 72 hours**

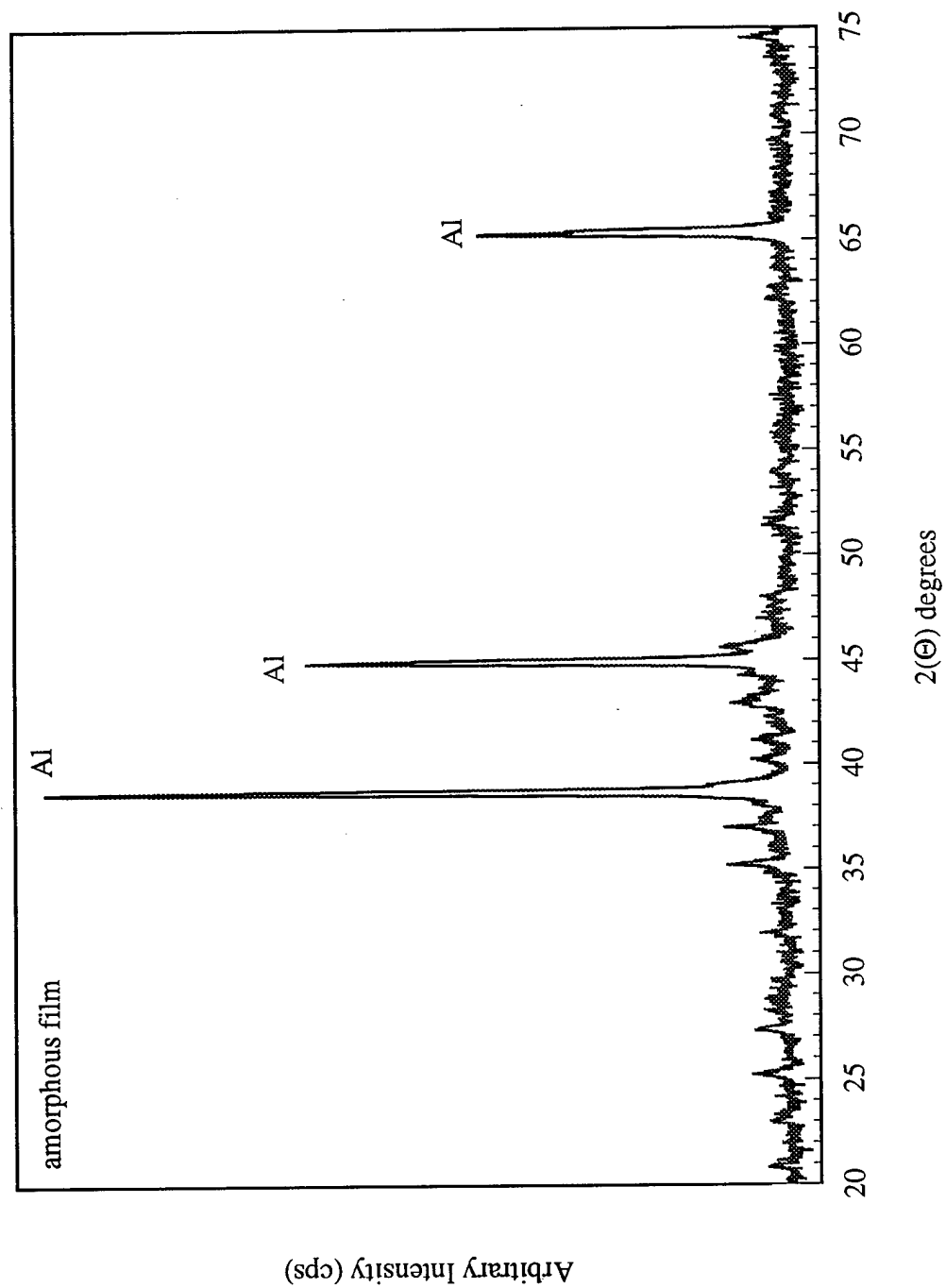


Figure 13.

precursors on the 2024 Al did eliminate the staining of the substrate; however, a noticeable increase in the viscosity of the solution was observed. SEM/EDS analysis show the formation of a 1.5  $\mu\text{m}$  thin film on the Al surface containing Ce on the surface of the 2024 Al after 3 coatings of the solution prepared at 75°C for 96 hours (Figures 14 and 15). Further analysis by x-ray diffraction revealed that the films had crystallized into the  $\text{CeO}_2$  structure after the 150°C anneal (Figure 16). This film was observed to have particles on the order of 10 - 20nm, and were also found to be highly strained. Application of one coating of the 144 hr solution resulted in a film approximately 5.0  $\mu\text{m}$  thick which were extensively cracked (Figure 17). Figures 18 and 19 show the development of the  $\text{CeO}_2$  as a function of the solution time at 75°C.  $\text{CeO}_2$  is observable after 96 hours. It is believed that these  $\text{CeO}_2$  films form when the films were allowed to dry and dehydrate at 75°C. When heated to 150°C the ethylene glycol, which has a flash point of 110°C, is exothermic enough to allow the formation of the  $\text{CeO}_2$ . However, this does appear to occur at the expense of the structural integrity of the film.

It is apparent that the formation of the an amorphous Ce or crystallized  $\text{CeO}_2$  film is dependent largely on the viscosity of the solution. This viscosity change is believed to be due to the further polymerization of the ethylene glycol solution. Currently, attempts are being made to classify the variables associated with the formation of the  $\text{CeO}_2$  films so as to retain the integrity of the film. This should allow the possibility of testing the effects/benefits of either an elemental amorphous Ce film to provide electrochemical protection of the Al, or a  $\text{CeO}_2$  barrier film that can protect the Al.

#### **Preparation of Alumoxane-Ethylene Glycol Coating Solutions**

Initial work has found that the gluconato-alumoxane is soluble in an ethylene glycol solution with the aid of nitric acid. A solution containing 40 g of ethylene glycol and 1.0 ml  $\text{HNO}_3$  was heated to 50°C. The gluconato-alumoxane (5.0) g was added incrementally until most of the material was dissolved. The solution was then pressure filtered at 50°C, and it was subsequently observed that the undissolved material then went into solution. Initial experiments indicate that this solution readily wets the Al substrates. Initial spin coating have begun on 7075 Al substrates. The fabrication of Ce/Mo metal exchanged alumina oxide films using the carboxylato-alumoxanes will be evaluated using the alumoxane-ethylene glycol approach.

#### **4. References**

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3 CeO<sub>2</sub> coatings on 2024 Al substrate  
150°C anneal temperature between coatings

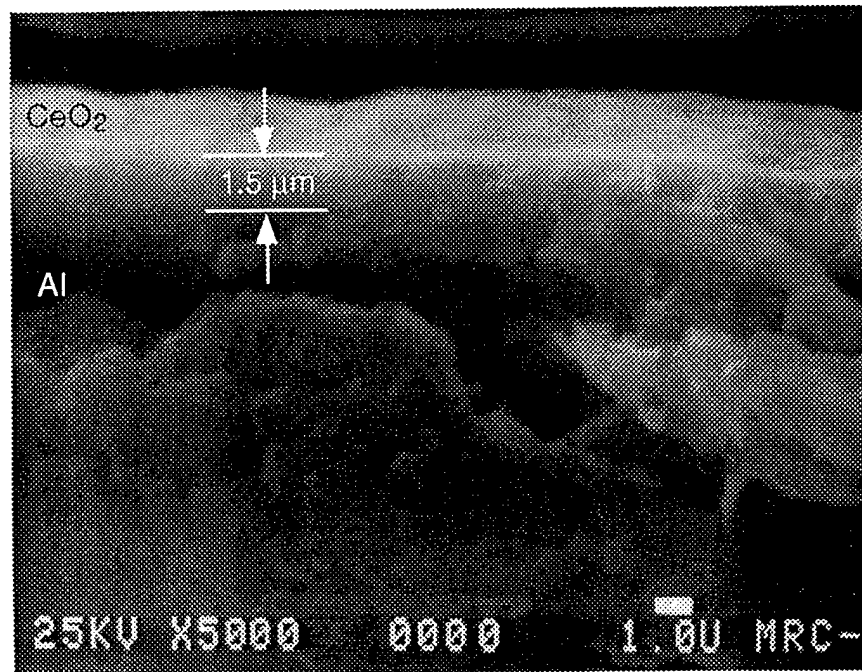
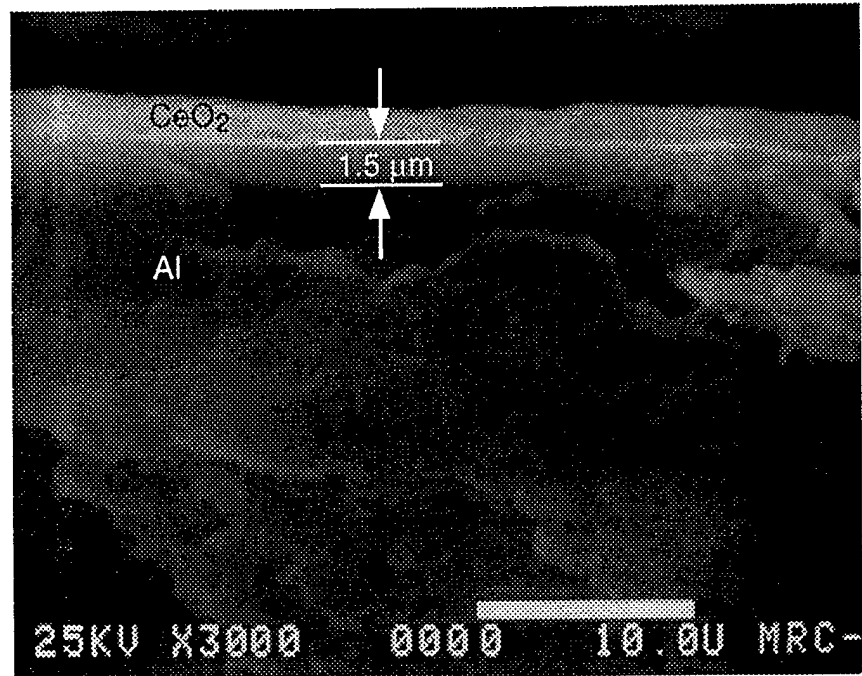


Figure 14.

3 CeO<sub>2</sub> coatings on 2024 Al substrate.  
150°C anneal temperature between coatings

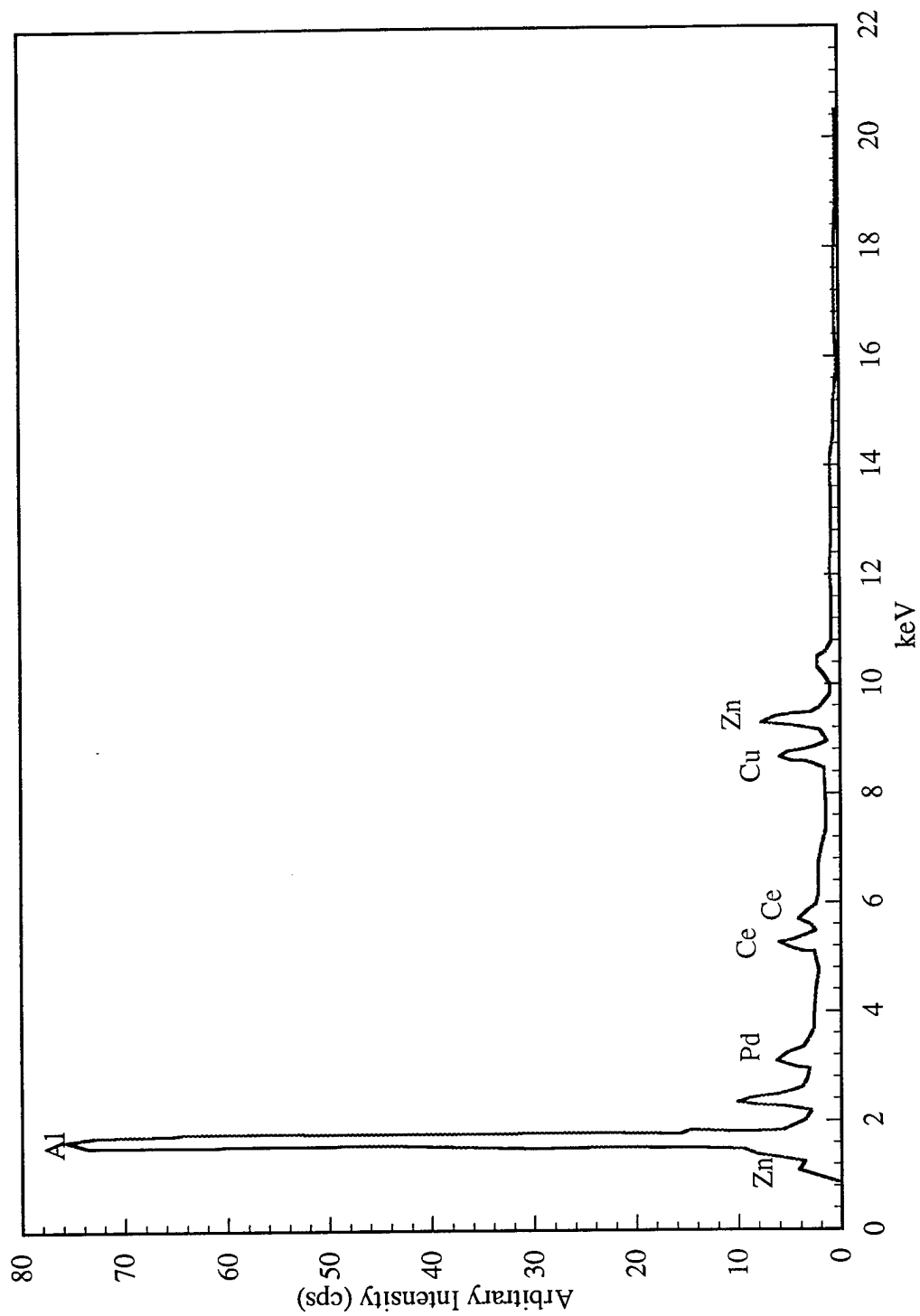


Figure 15.



**XRD Pattern of 3 CeO<sub>2</sub> coatings on 2024 Al substrate**  
**150°C anneal temperature between each coating.**

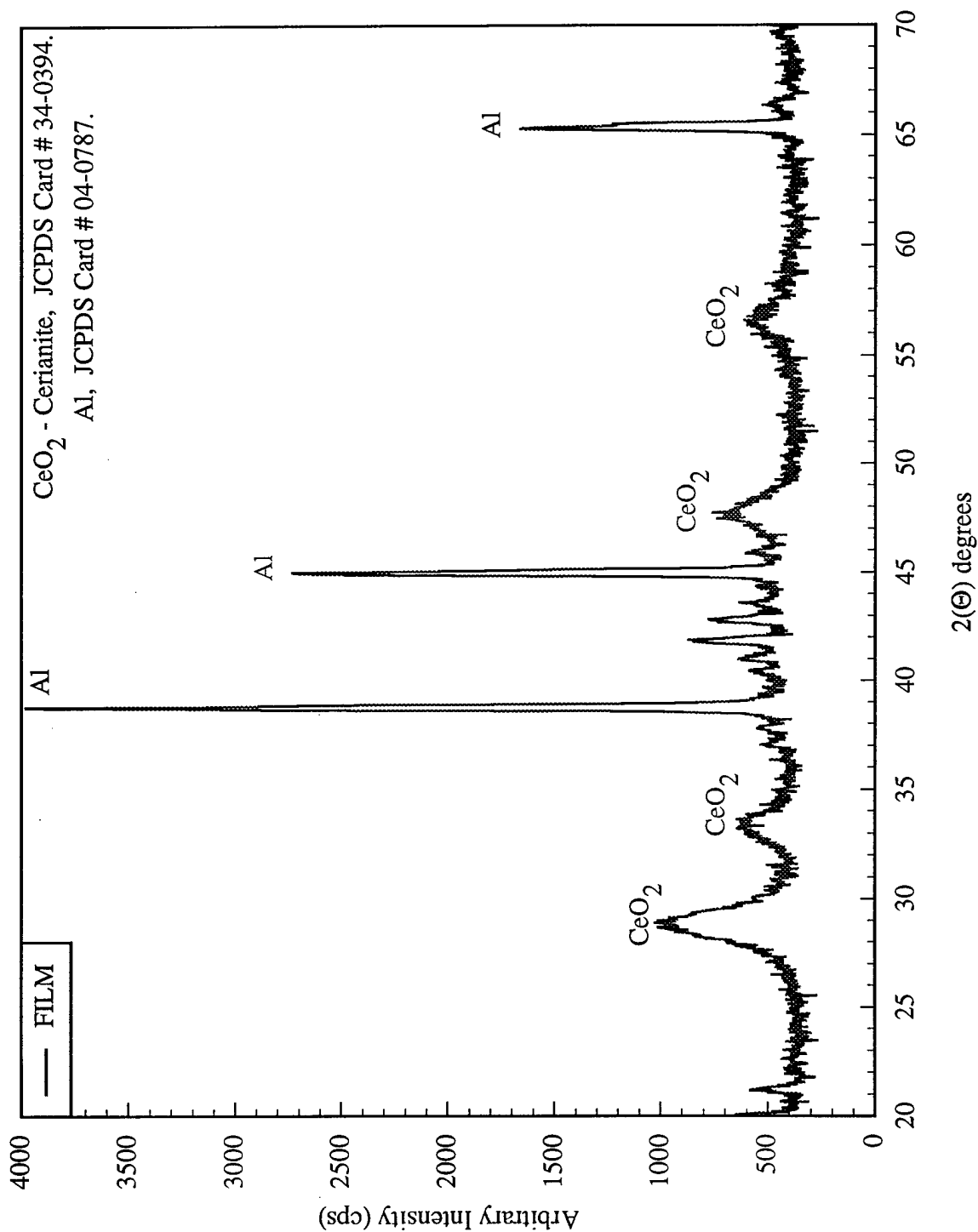
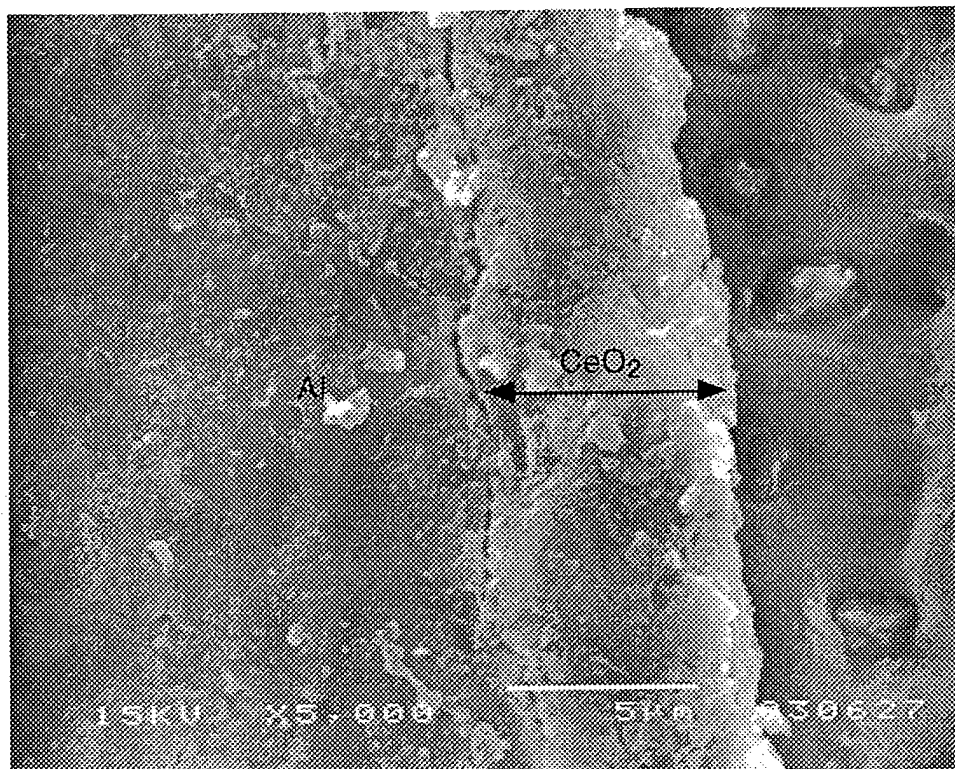
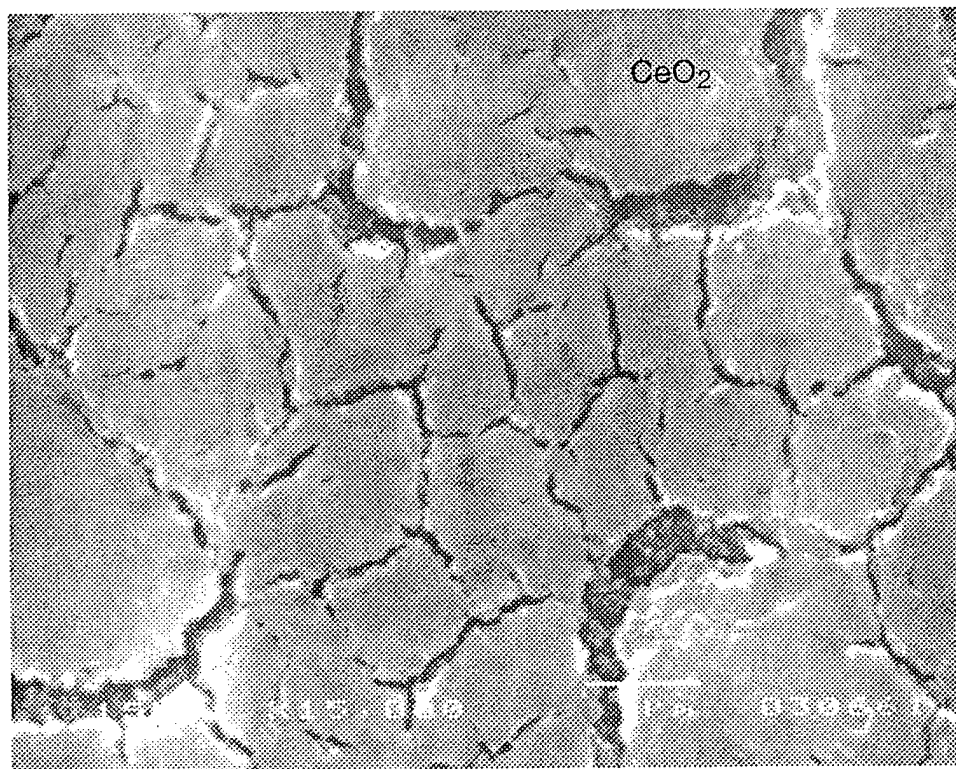


Figure 16.

1 CeO<sub>2</sub> layer on 2024 Al  
solution prepared at 75°C for 144 hours



Cross-Section



Top

Figure 17.

Effect of precursor heat treatment on  
CeO<sub>2</sub> development

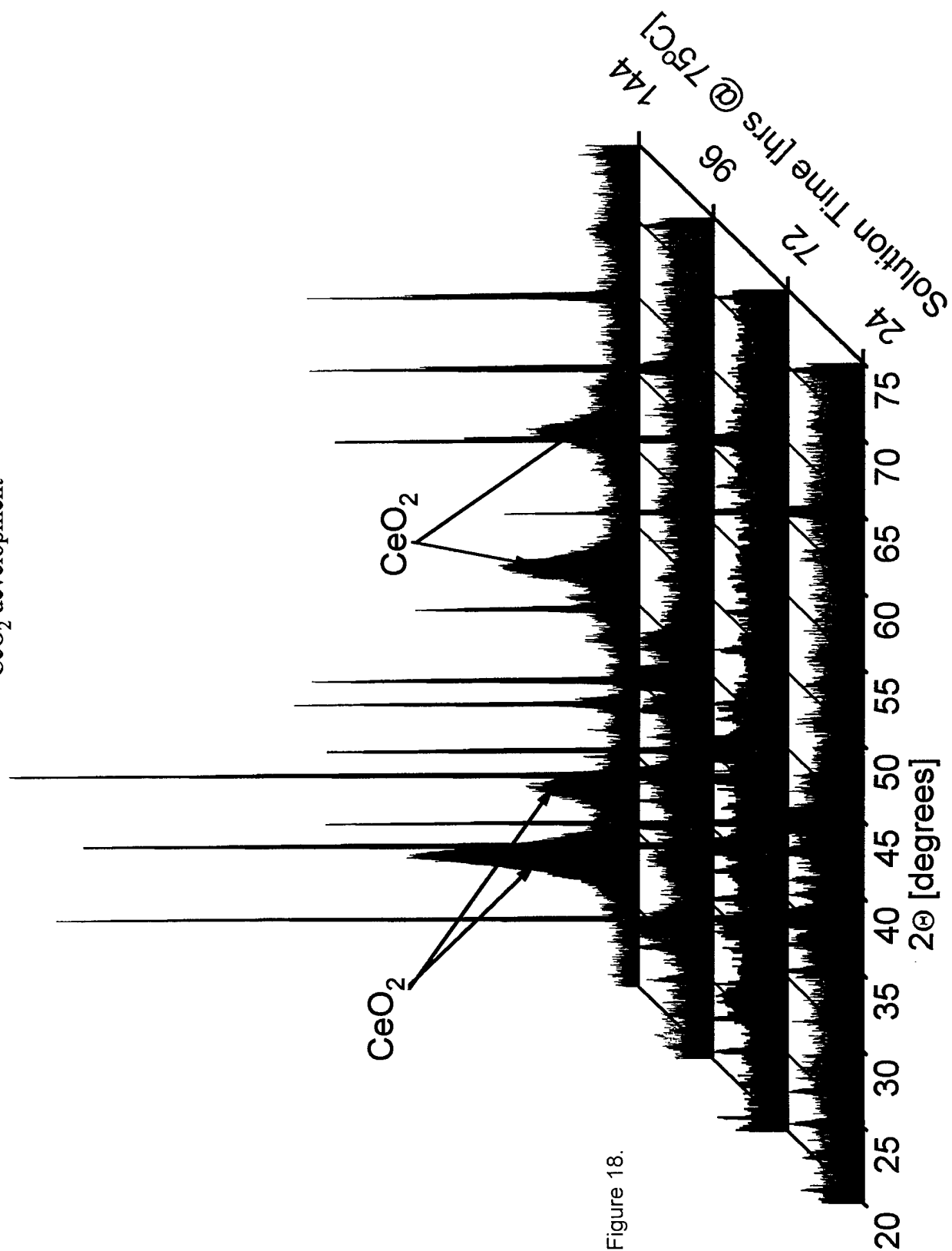
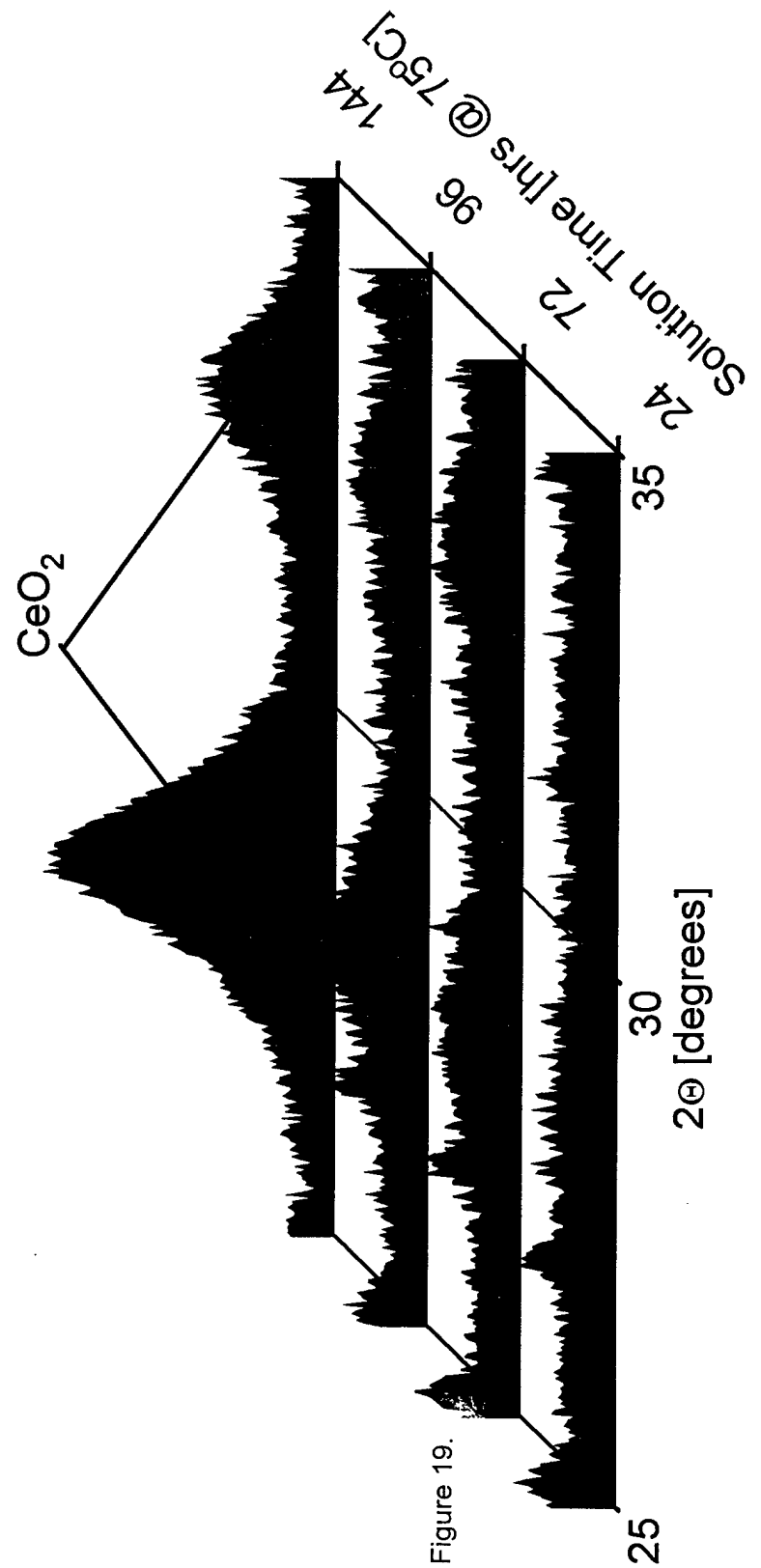


Figure 18.

Effect of precursor heat treatment on  
 $\text{CeO}_2$  development 25 - 35° 2 $\theta$  section



## **Appendix 1: EIS Results from Alumoxane Containing Coatings**

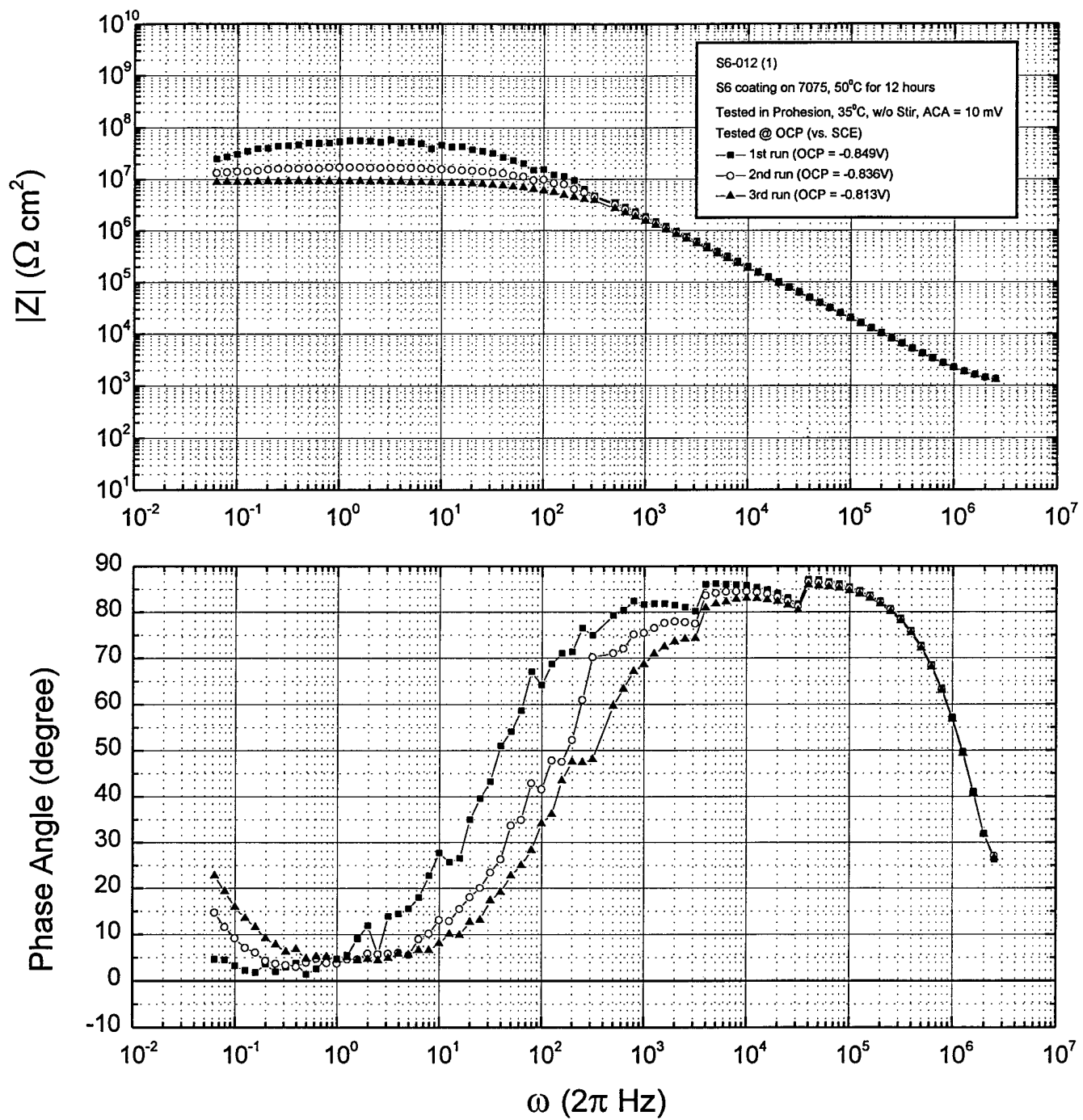


Figure 1.

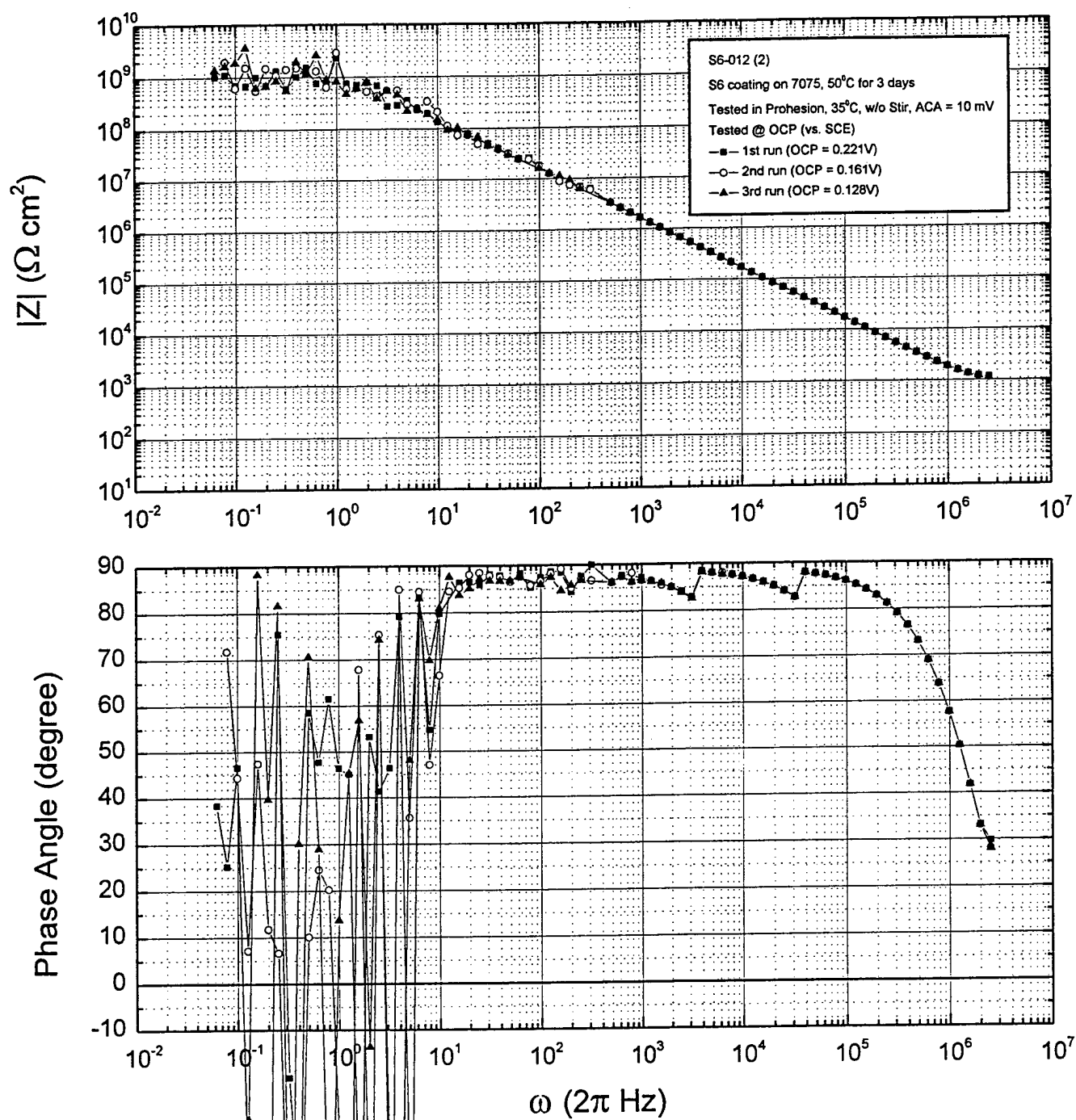


Figure 2

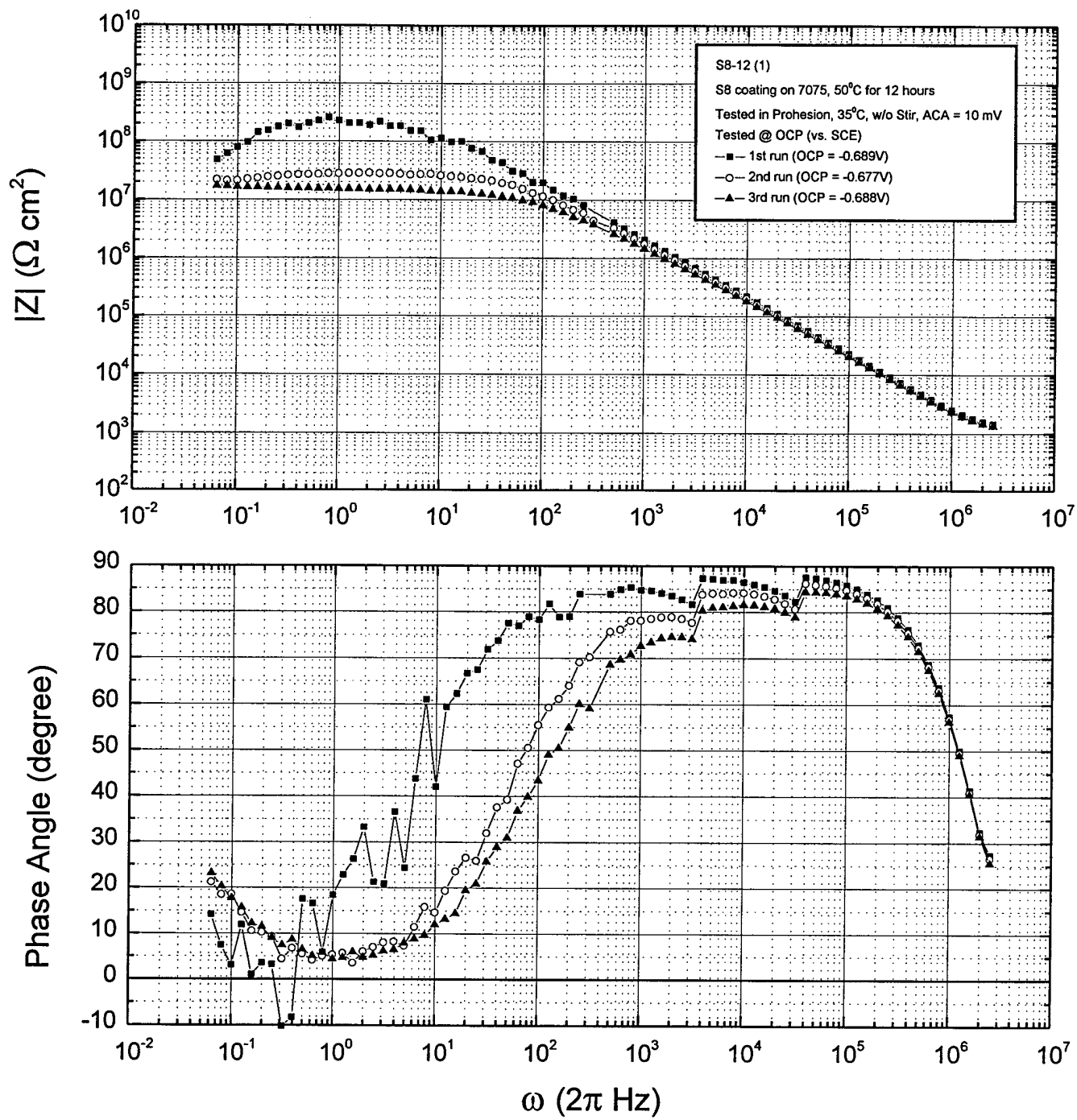


Figure 5